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Assessing membrane biofouling and its gel layer of anoxic/oxic membrane bioreactor for megacity municipal wastewater treatment during plum rain season in Yangtze River Delta, China

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ABSTRACT

This study assessed membrane biofouling and its gel layer of anoxic/oxic membrane bioreactor (A/O-MBR) for megacity municipal wastewater treatment during plum rain season, which was continuous rainy weather, in Yangtze River Delta, China. A laboratory-scale A/O-MBR was operated to treat the municipal wastewater from Quyang wastewater treatment plant, which located at the typical megacity of Shanghai in Yangtze River Delta, from April to July accompanying with plum rain season. As reactor performance showed, COD_{Cr}, NH_4^+-N, TN, TP of the influent gradually decreased during plum rain season, and inhibited pollutant removal due to organic carbon shortage. However, dissolve inorganic carbon and inorganic components in mixed liquid had an obvious increase under rainy weather. Membrane filtration results indicated that plum rain season enhanced pore blocking behavior, further leading to the serious membrane biofouling but inhibiting gel layer formation. Additionally, gel layer analysis predicted that plum rain season led to plenty of inorganic components and precipitate flew into A/O-MBR reactor. Inorganic components with elements of Ca, Mg Ba, Fe, Al and Si seriously blocked membrane pores. Those components also accumulated into gel layer in the form of SiO_2, $CaCO_3$, $CaSiO_3$, $MgNH_4PO_4$, $BaCO_3$, $AlPO_4$, etc. Consequently, plum rain season enhanced pore blocking behavior and led to severe membrane biofouling but with the inhibition of gel layer formation.

1. Introduction

With over 30-years economic development, megacities, containing over millions population, have been built up all over the China, such as Beijing, Shanghai, Shenzhen, Guangzhou, Chengdu, Wuhan, Changsha, Suzhou, etc. Especially, Yangtze River Delta contains Shanghai and parts of Jiangsu, Zhejiang and Anhui provinces, which is the economic and industrial center of China (Chong et al., 2016; Gao et al., 2017). Thus, dozens of megacities, Shanghai (24 million population), Suzhou (13 million population), Nanjing (8.3 million population), Hangzhou (9.0 million population), Changzhou (4.7 million population), Hefei (7.9 million population), Wuxi (6.5 million population), etc. were located in the region of Yangtze River Delta, promoting the formation of Yangtze River Delta urban agglomerations (Li et al., 2016).

However, huge population of megacities induced the serious pollution pressure to municipal wastewater treatment plant, and environmental risk of megacities, especially Yangtze River Delta, have been attracted more attentions in recent years (An et al., 2015; Kang et al., 2016; Zhuo et al., 2017). Thus high efficiency municipal wastewater treatment technology is required. Membrane bioreactor (MBR), combining physical separation and biological degradation, is a high-efficiency technology for wastewater treatment and water reuse (Aslam et al., 2017; Eyvaz et al., 2016; Navarro et al., 2016; Torretta et al., 2017). In recent decades, because of the outstanding advantages, such as sludge maintainment, low footprint, less sludge production, high quality of effluent, etc., MBR has been widely applied in China (Meng et al., 2017). There are dozens

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of installations of large-scale MBR for >10,000 m^3/d municipal wastewater treatment in China, and parts of them were mainly located at megacities of Yangtze River Delta, China (Huang et al., 2010; Shen et al., 2012). Hu et al. (2014) also reported that over 6 municipal wastewater treatment plants in Wuxi were applied with MBR technology. Consequently, MBR is one of the best effective technology for megacity municipal wastewater treatment, especially space-limiting area.

However, membrane biofouling, as the obstacle for the widespread application of MBR, usually occurs with pore blocking and the gel-like layer formation on membrane surface (Wang et al., 2008; Wang and Wu, 2009). Gel-like layer is normally classified into gel layer (mainly caused by solutes, colloids, extracellular polymeric substances (EPS), etc.) and cake layer (attributed to the adhesion and accumulation of cake sludge, inorganic particles, etc.), and recent study (Hong et al., 2014) reported that formation of both gel layer and cake layer simultaneously occurred on membrane surface during MBR operation. In addition, during MBR operation in practice, membrane was applied under sub-critical flux to mitigate severe cake layer formation on membrane surface, and membrane was generally fouled with a thin gel-like layer and then operated with physical and/or chemical washing to extend the membrane lifetime (Guo et al., 2012; Huang et al., 2010; Wang et al., 2008). This thin gel-like layer, which is attributed to the adhesion of solutes, colloids, EPS (majority) and the accumulation of cake sludge, inorganic particles (minority), is the key contribution for membrane biofouling, and this thin gel-like layer was called as gel layer in this study.

Yangtze River Delta annually has a continuously rainy weather from late spring to early summer, which is commonly called plum rain season. Plum rain season normally begins from the middle of June, and ends at the beginning of July, lasting for approximately 20-plus days. According to previous literature (Sun et al. 2010, 2015), municipal wastewater treatment system of megacities in Yangtze River Delta would show obvious performance variations on pollution removal because of the influent evolution with rainy weather. Tsai et al. (2011) predicted that acid rainfall caused plenty of inorganic components, such as NH_4^+, HCO_3^-, Na^+, Ca^{2+}, etc., dissolved into the influent of wastewater treatment system during plum rain season. Zhou et al. (2015a) also reported that lots of inorganic components from constructions or its waste easily flew into municipal wastewater plants with rainfall in megacity. On the other side, recent researches (Meng et al., 2017; Zhou et al., 2014, 2017c) proved that inorganic components play a significant role in gel layer formation and membrane biofouling. Thus, it could be speculated that plum rain season might have some effects on membrane biofouling and its gel layer of MBR, especially for megacity municipal wastewater treatment. However, this speculation have never been studied.

This study aimed to assess membrane biofouling and its gel layer of anoxic/oxic MBR (A/O-MBR) for megacity municipal wastewater treatment during plum rain season in Yangtze River Delta, China. A laboratory-scale A/O-MBR was set-up and operated to treat the municipal wastewater from Quyang wastewater treatment plant, which located at the typical megacity of Shanghai in Yangtze River Delta, from April to July accompanying with plum rain season. Temperature was in the range of 22–36 °C during the entire operation, and this temperature variation would not induce obvious effects on membrane biofouling based on previous study (Miyoshi et al., 2009). Thus, this study ignored the temperature effects on membrane biofouling. In this study, various measurements, such as XRD (X-ray diffraction), SEM-EDX (scanning electron microscopy-energy dispersive X-ray analyzer), membrane resistance, EPS of gel layer, etc., were carried out to analyze membrane biofouling and identify its gel layer properties.

2. Materials and methods

2.1. Set-up and operation of A/O-MBR

A laboratory-scale A/O-MBR, containing a working volume of 4.5 L (anoxic and oxic zones of 1.5 L and 3.0 L, respectively), was operated from April to July. A PVDF (polyvinylidene fluoride) hollow fiber membrane module (with a total surface area of 260 cm^2; 0.4 μm pore size; Litree Company, China) was installed in the oxic zone. A constant fluid flux was set at 17 L/(m^2 h) with intermittent suction mode (10 min suction and 2 min relaxation per cycle) was applied during operation. Pressure gauge was used for *trans*-membrane pressure (TMP) measurement. The flow rate of recycled mixed liquor from the oxic zone to the anoxic zone was controlled at 200% of the influent flow rate. pH in the reactor was controlled by NaOH and HCl addition within the range of 7.0–7.7. Hydraulic retention time (HRT) and solids retention time (SRT) were maintained at 10.0 h and 30 days, respectively. When TMP reached 40 kPa, the membrane module was removed for physical (washing with tap water) and chemical cleaning (1% NaOCl and 10% citric acid immersion for 6 h, respectively) to recover the membrane permeability.

The specific aeration demand per membrane area (SADm) in some full-scale MBRs is generally ranged 0.2–1 m^3 air/m^2 h. However, according to previous studies (Wang et al. 2008, 2010), pilot-scale MBRs for megacity (Shanghai, China) municipal wastewater treatment in Yangtze River Delta remained a high SADm (approximately 8.6–35 m^3 air/m^2 h), even with sheet membrane module. Hu et al. (2014) and its references showed that large-scale MBRs for megacity (Wuxi, China) municipal wastewater treatment with hollow fiber membrane module also needed high SADm to induce the effective scouring with a cross-flow action for the inhibition of cake sludge accumulation on membrane surface. Especially, Chengbei WWTP, the largest scale MBR (50,000 m^3/d; with hollow fiber membrane module) in Wuxi, maintained approximately 13–17 m^3 air/m^2 h SADm during operation. Thus, MBR operational conditions for megacities in Yangtze River Delta were different from other areas, especially high aeration rate. In addition, because of the small reactor volume and high mixed liquid concentration, high SADm (>13 m^3 air/m^2 h) was necessary for prevention of bubbling pore blocking. Consequently, this study applied a high SADm (approximately 15 m^3 air/m^2 h) to simulate large-scale MBR operation, and the air diffuser was set for supplying continuously air (0.4 m^3/h; controlling with gas flow-meter) to offer oxygen for microbial activity and induce a cross-flow action for effective scouring.

The influent of this A/O-MBR was the effluent from an aerated grit chamber of the Quyang municipal wastewater treatment plant (WWTP) (31°16′ N, 121°28′ E, Shanghai, China; Fig. S1). Quyang WWTP, built up at 1982, locates at the downtown of Shanghai (Hongkou district) with total occupied space of 3.54 ha. Quyang WWTP serves over 650 ha residential area with 200 thousands people, which is in the system of mixture of rainwater and sewerage. To better modify the practical operation, the inoculating biomass was drawn from the return activated sludge stream in Quyang WWTP. The newly inoculated A/O-MBR was initially operated to achieve steady state for the acclimatization of activated sludge. The membrane module was then replaced with a new unit and the A/O-MBR was operated for the experiments from April to July.

2.2. Membrane resistance analysis

Membrane resistance, which is a major characteristic for membrane biofouling, can be calculated as the following equation:

$$R_{total} = R_{membrane} + R_{pore\ blocking} + R_{gel\ layer} \quad (1)$$

$$R_n = \frac{\Delta P}{\mu J} \quad (2)$$

$R_{membrane}$ is the resistance of clean membrane, $R_{pore\ blocking}$ is the resistance due to pore blocking and $R_{gel\ layer}$ is the gel layer resistance. Resistance of concentration polarization was concluded as parts of $R_{gel\ layer}$ in this study (Meng et al., 2007). R_n is the *total*, *membrane*, *pore blocking* or *gel layer*. ΔP is TMP, J is permeate flux, μ is viscosity of the permeate water (μ was measured with DV-C viscometer (Brookfield, USA)). R_{total} is the value summation of $R_{membrane}$, $R_{pore\ blocking}$ and $R_{gel\ layer}$.

2.3. Extraction and measurement of EPS in gel layer

EPS in gel layer was extracted based on a modified thermal extraction method (Zhou et al., 2017c). 0.5 g gel layer was re-suspended with 10 ml 0.9% NaCl solution, and shaken at 150 rpm for 10 min after 15 min ultrasound treatment (DS510DT, 40 kHz, 300 W, Shangchao, China). Then the sample was heated at 80 °C for 30 min. Next, sludge was centrifuged (MILTIFUGE X1R, Thermo Electron Corporation, USA) at 12,000 g for 20 min, and the supernatant was regarded as EPS. EPS were normalized as the concentration of polysaccharide, protein, nucleic acid and humic acid (all organic components represented as TOC). They were measured by the phenol-sulfuric acid method, Branford method, diphenylamine method and TOC analyzer (TOC-V_{VPN}, Shimadzu, Japan), respectively.

2.4. Other analysis

The standard methods (APHA, 1998) were used to measure concentrations of NH_4^+-N, COD, TN, TP, dissolve inorganic carbon (DIC), suspended solid (SS), mixed liquor suspended solid (MLSS) and mixed liquor volatile suspended solids (MLVSS). A focused beam reflectance measurement (Eyetech particle size and shape analyzer, Ankersmid, Holland) was used to identify the particle size of sludge. DO and pH were measured with a DO-and-pH meter (HQ4d, HACH, USA). Inorganic elements in gel layer were detected with an inductively coupled plasma-optical emission spectrometer according to the Standard Methods (China-NEPA, 2002). Before SEM (XL30, Philips, Netherlands)-EDX (Oxford Isis, UK) measurement, a piece of the membrane was cut from the middle section of the membrane module and frozen in liquid-nitrogen. Oxygen uptake rate (OUR) was applied as Zhou et al. (2017b).

3. Results and discussion

3.1. Treatment performance variations during plum rain season

Fig. 1 separately shows treatment performance variations of A/O-MBR for COD, NH_4^+-N, TN, TP, DIC and SS from April to July with plum rain season. It is obvious that COD_{Cr}, NH_4^+-N, TN, TP of the influent gradually decreased under rainy weather during plum rain season (Fig. 1(a)–(d)). Hu et al. (2014) and Sun et al. (2015) both showed that the large-scale MBRs treating municipal wastewater in Heifei and Wuxi, which were megacities containing approximately 7.9 and 6.5 million population in Yangtze River Delta, respectively, had the similar gradual decrease of pollutants in the influent during plum rain season. Thus, the rainy weather during plum rain season would cause an obvious variation with pollutants decrease. In addition, plum rain season also weakened the pollutants removal of A/O-MBR. Especially at 2-June, COD_{Cr} and NH_4^+-N in the effluent suddenly increased to over 90 and 10 mg/L, respectively, further illuminating that plum rain season inhibited the pollutant degradation of sludge in A/O-MBR. During plum rain season, A/O-MBR had partly restrained the NH_4^+-N removal. Hu et al. (2014) also reported that MBR in Hefei WWTP had the poor performance during plum rain season. Moreover, removal efficiencies of TN and TP were in the range of 50–70% and 55–65%, respectively, before rainy weather, but they decreased to 20–30% and 30–40% during plum rain season, respectively, because of organic carbon shortage (Sun et al., 2010; Zhang et al., 2016).

Dissolve inorganic carbon was also analyzed during the entire operation (Fig. 1(e)). DIC in the influent was only 3–8 mg/L during 4-April to 15-May, but it began to increase rapidly to over 20 mg/L from 15-May and maintained around 20–25 mg/L. It was because megacity of Yangtze River Delta, containing lots of cement building, were in the serious acid rain area, and rainy weather led to the construction corrosion and plenty of DIC flowing into WWTP. Additionally, only 2–5 mg/L DIC was remained in the reactor before plum rain season, but over 10 mg/L DIC was obstructed in A/O-MBR during rainy weather, meaning that plum rain season caused DIC maintainment in A/O-MBR system. Additionally, SS ranged around 100–600 mg/L during most of the operation (Fig. 1(f)). SS in the effluent is 0 mg/L due to the intercept of membrane module, indicating all of SS was remained in the reactor.

Fig. 2 presents that reactor MLSS ranged from 5 to 7 g/L before 15-May, but it decreased gradually with influent COD_{Cr} drop during plum rain season. OUR, which is the index for sludge viability, had a similar dropping tendency as MLSS. In addition, MLVSS/MLSS ratio had an obvious decease with plenty of DIC interrupt in the reactor, indicating bacterial drop in the sludge. Based on Michaelis-Menten kinetics, the concentration of substrate is positively related with the enzyme reaction. Thus, low COD_{Cr} with rainy weather directly reduced the enzyme reaction of bacterial metabolism, and slowed down the sludge growth, causing MLVSS decrease and sludge viability inhibition. Moreover, plum rain season led to lots of DIC maintained in the reactor, straightly reducing MLVSS/MLSS ratio.

3.2. Membrane filtration

TMP is the significant index for presenting membrane filtration, and its development rate directly shows the extent of membrane biofouling. Fig. 3 shows the TMP variations of reactor from 6-Apr to 14-Jul. TMP variation could be classified into 6 phases. Phase 1 and Phase 2 presented TMP development before plum rain season, and Phase 3 was the period when the weather was beginning to be in the stage of continuously rainy for plum rain season. Phase 4, 5 and 6 were the membrane filtration performance during plum rain season, especially a fresh new membrane module was switched at Phase 6 for re-verify the effects of plum rain season on the membrane filtration. Before plum rain season, TMP development rates during Phase 1 and 2 were 1.45 and 1.67 kPa/d, respectively. Phase 3 had a rapid TMP growth with 1.78 kPa/d when it started to be continuously rainy. Furthermore, Phase 4 and 5 had the high TMP development rate with 2.68 and 3.16 kPa/d, respectively, during plum rain season. Even having been switched a fresh new membrane module, A/O-MBR still had a 2.86 kPa/d TMP development rate. This phenomenon indicated that plum rain season induced the serious membrane biofouling and inhibited membrane filtration. In addition, Fig. S2 shows that critical flux value of membrane module was decreased with plum rain season, indicating the poor sludge filterability under rainy weather. Van den Broeck et al. (2011) and Zhang et al. (2015) reported that sludge filterability had a close positive relationship with EPS, inorganic particles, colloids, etc., which had been considered as biofouling-causing substances. Thus, poor sludge filterability should make a contribution toward severer

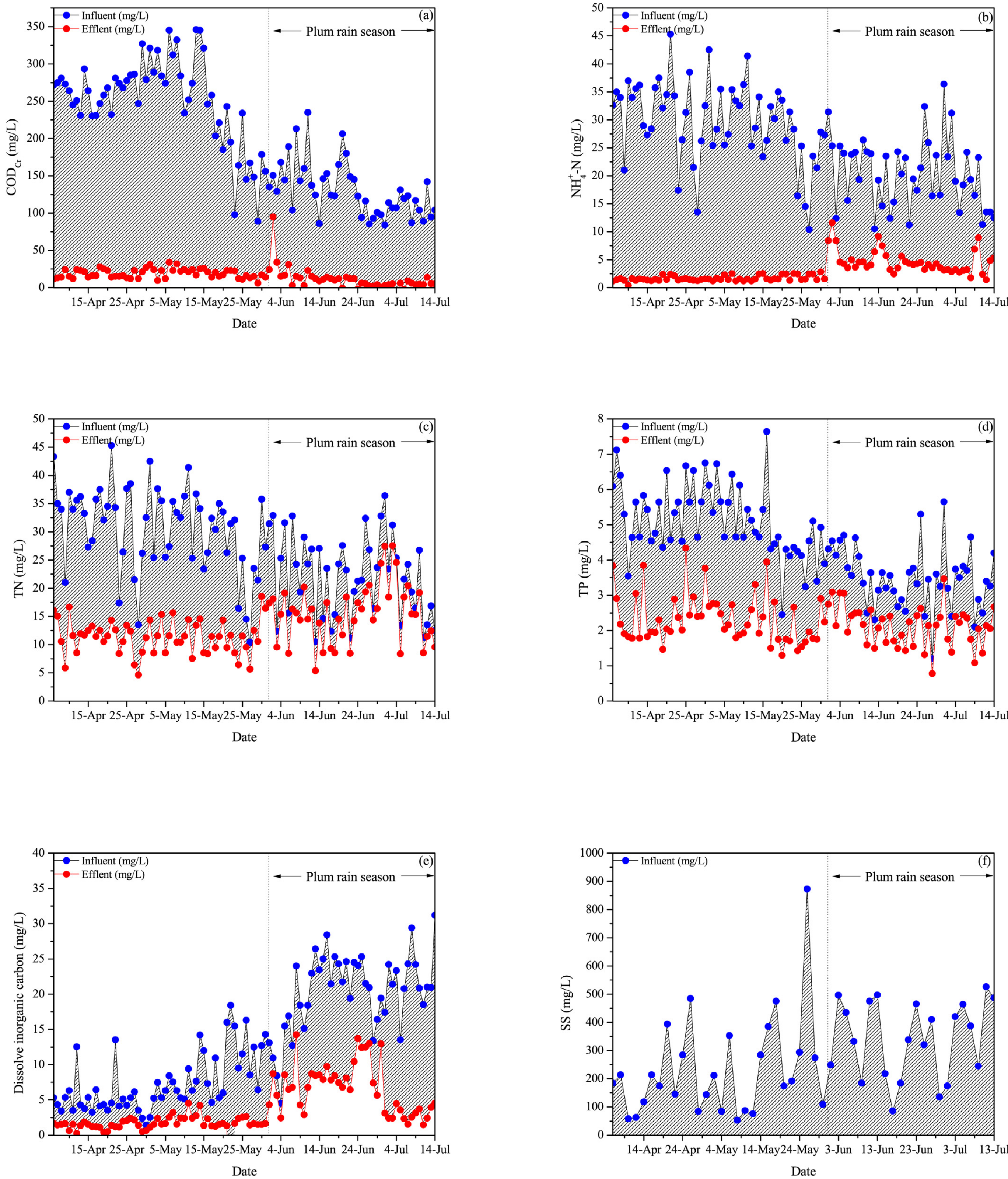

Fig. 1. Pollutant removal variations of A/O-MBR during plum rain season: (a) COD; (b) NH_4^+-N; (c) TN; (d) TP; (e) dissolve inorganic carbon; (f) influent SS.

membrane biofouling during plum rain season.

Membrane biofouling resistance was also carried out to further analyze the membrane biofouling during plum rain season. Total membrane biofouling resistance can be classified into clean membrane resistance, pore blocking resistance and gel layer resistance. Table 1 shows that total membrane biofouling resistance had a certain of increase from 2.65 to 3.24 10^{12} m^{-1} with plum rain season, which was consistent with Fig. 3 and further proved the

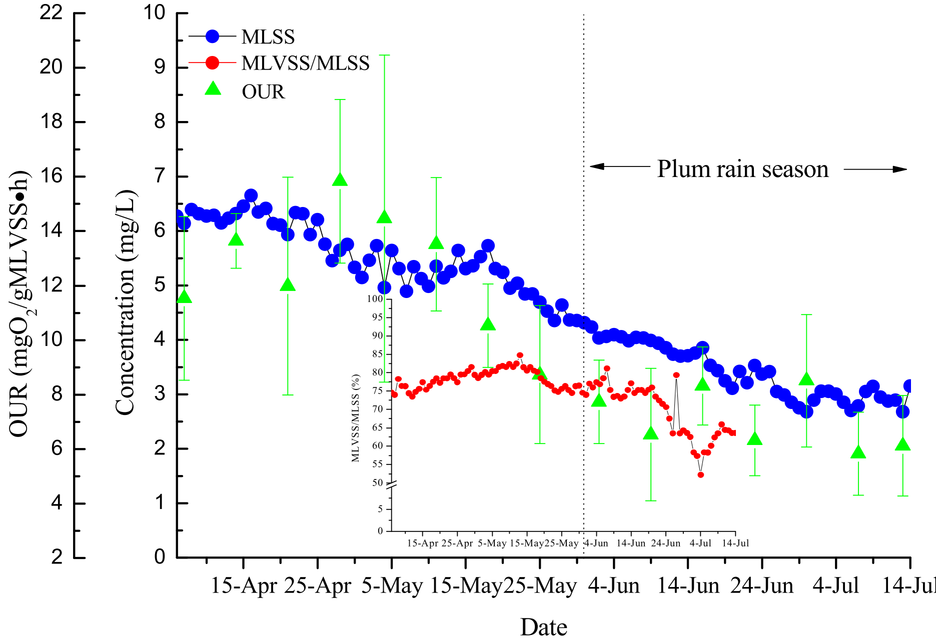

Fig. 2. Variations of MLSS and MLVSS/MLSS ratio in A/O-MBR during plum rain season.

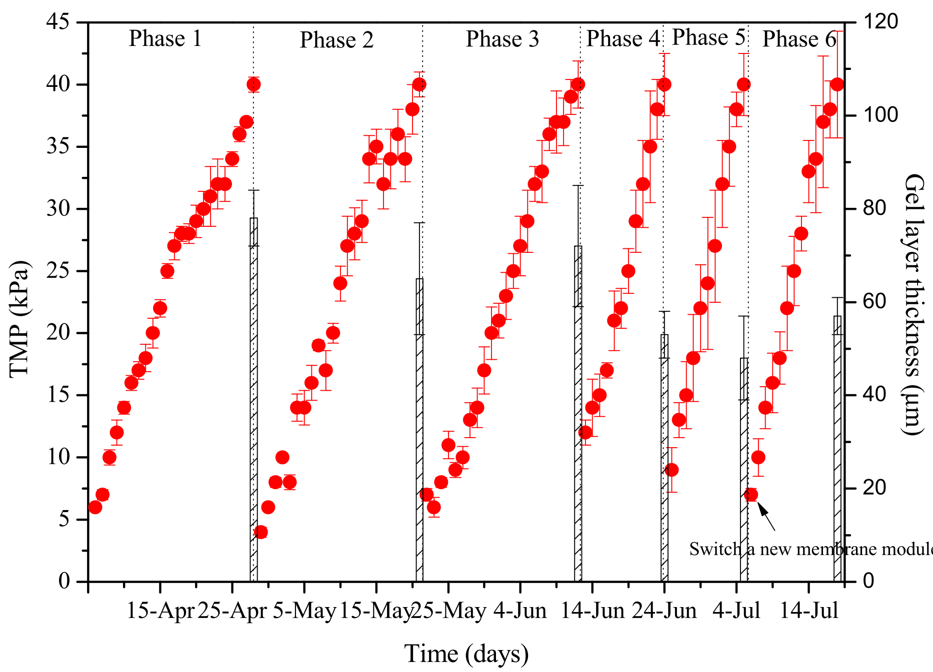

Fig. 3. Variations of TMP and gel layer thickness during plum rain season.

severer membrane biofouling with plum rain season in the megacity at Yangtze River Delta, China. Additionally, previous studies (Guo et al., 2012; Wang et al., 2011) showed that higher biofouling behavior caused over 90% contribution of cake sludge accumulation to total membrane resistance. However, obvious cake sludge accumulation on membrane surface would enhance MBR operation cost, and need advance membrane washing. Thus, during some pilot or large scale MBRs operation, only thin gel-like layer (which was called “gel layer” in this study) developed on membrane surface, and then membrane module was cleaned for membrane reapplication, such as Guo et al. (2008). Wu et al. (2011) and Wang et al. (2008) also reported that gel layer resistance would not obviously higher than pore blocking resistance when thin gel layer development, which was consonant with Table 1 result. Thus, Guo et al. (2008) showed the similar result of membrane resistance distribution as this study. In addition, high SADm effectively mitigated cake sludge accumulation on to membrane surface, reducing gel layer contribution to total biofouling (Guo et al., 2012; Meng et al., 2017).

Based on Table 1, it was normal that gel layer resistance was the major part of membrane biofouling resistance during Phase 1, 2 and 3. However, with the rainy weather during plum rain season, pore

Table 1
Membrane biofouling resistances during plum rain season.

	Resistance	R_{total}	R_m	R_p	R_c
Phase 1	Value (10^{12} m^{-1})	2.65	0.50	0.98	1.17
	Percentage (%)	100	19	37	44
Phase 2	Value (10^{12} m^{-1})	2.73	0.51	0.91	1.31
	Percentage (%)	100	19	33	48
Phase 3	Value (10^{12} m^{-1})	2.95	0.49	1.10	1.36
	Percentage (%)	100	17	37	46
Phase 4	Value (10^{12} m^{-1})	3.10	0.52	1.40	1.18
	Percentage (%)	100	17	45	38
Phase 5	Value (10^{12} m^{-1})	3.24	0.48	1.47	1.29
	Percentage (%)	100	15	45	40
Phase 6	Value (10^{12} m^{-1})	2.96	0.47	1.38	1.11
	Percentage (%)	100	16	47	38

blocking resistance replaced gel layer resistance as the majority of membrane biofouling, indicating that plum rain season enhanced pore blocking behavior during membrane biofouling. Moreover, Fig. S3 shows the decrease of sludge particle size with plum rain season, and many literature (Guo et al., 2012; Meng et al., 2017) have reported small size sludge particles would block the membrane pore during membrane filtration. Above results (Fig. 2) also showed that inorganic components increased with plum rain season. Consequently, increasing small-size particles in sludge promoted the pore blocking behavior, and further enhanced the membrane biofouling with rainy weather during plum rain season.

3.3. Gel layer properties

Gel layer is considered as the major role in membrane biofouling, inducing most of biofouling behaviors (Aslam et al., 2017; Krzeminski et al., 2017; Zhou et al., 2017a). Identification of gel layer, especially ones during Phase 2 and Phase 5, which were representative membrane biofouling performance without and with plum rain season, was carried out in this Section. Fig. 4 shows the SEM image (1000×) of the gel layer surface during Phase 2 and Phase 5. Gel layer of Phase 5 obviously contained more particles than that of Phase 2, indicating that more particles accumulated into gel layer. Additionally, corner angle shape of most of particles on gel layer surface partly predicted their inorganic structure, and XRD results (Table S1; most of particles had high percentage of element Ca, Mg, Fe, Ba, Al, Si, etc.) further proved the most of them were inorganic particles. It means that more inorganic particles contributed to gel layer formation with plum rain season, which should be because of the increasing inorganic components in the influent with rainy weather. In addition, gel layer thickness at the end of filtration (TMP = 40 kPa) of each phases was analyzed with SEM. Fig. 3 shows that gel layer thickness of Phase 1, 2 and 3 were 10–20 μm thicker than that of Phase 4, 5 and 6, indicating that plum rain season reduced the gel layer thickness. Based on previous studies (Wang and Waite, 2009; Wang et al., 2008; Xu et al., 2015), EPS, containing bacteria, inorganic particles, etc., in mixed liquid contributed the formation of gel layer, and gel layer thickness directly associated with MLSS. Thus, low MLSS with plum rain season (Fig. 2) was one of major reasons for the decrease of gel lay thickness.

Organic components are considered as the majority of contribution for gel layer formation and membrane biofouling (Campo et al., 2017; Zhou et al., 2015b). Thus, EPS of gel layer was carried out to analyze the effects of plum rain season on membrane biofouling. Fig. 5 shows that protein and TOC of EPS in gel layer had a certain decrease with plum rain season, but polysaccharide in gel layer did not present an obvious variation under rainy weather. Polysaccharides and protein in the influent during each Phase were

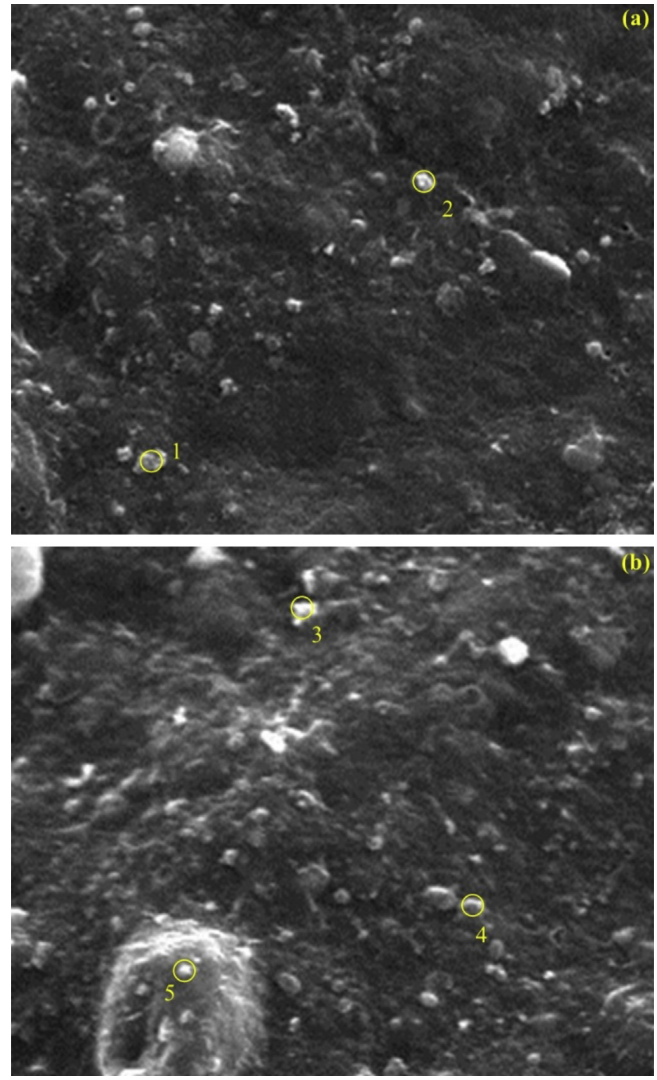

Fig. 4. SEM image (1000×) of gel layer surface when TMP = 40 kPa during (a) Phase 2 and (b) Phase 5.

lower than the minimum of measuring range. It indicated that polysaccharides and protein in the influent could be ignored, and polysaccharides and protein in gel layer should be contributed by bacteria in activated sludge. As Fig. 1 showed, various pollutants in the influent showed the obvious decrease during plum rain season, predicting the nutrient decrease for bacterial metabolism. Thus, nutrient decrease partly reduced the biomass in the mixed liquor (Fig. 2), which directly led to the decrease of extracellular secretion, especially protein (Zhou et al., 2017c). Consequently, the certain TOC decrease of EPS in gel layer with plum rain season partly because of the low nutrient in influent of municipal wastewater. On the other hands, Shen et al. (2012) had reported that polysaccharide and TOC, especially polysaccharide, were correlated significantly with membrane biofouling in large-scale MBRs, which were operated in plum rain season area, but protein did not present direct correlation with biofouling. Polysaccharide is further deemed as the key biofouling-causing substances during membrane filtration (Rosenberger et al., 2006; Zheng et al., 2010). Therefore, although plum rain season caused a certain of decrease of protein and TOC in gel layer, comparatively stable polysaccharide in gel layer would not induce obvious variations of membrane biofouling.

According to above results, inorganic components largely flew

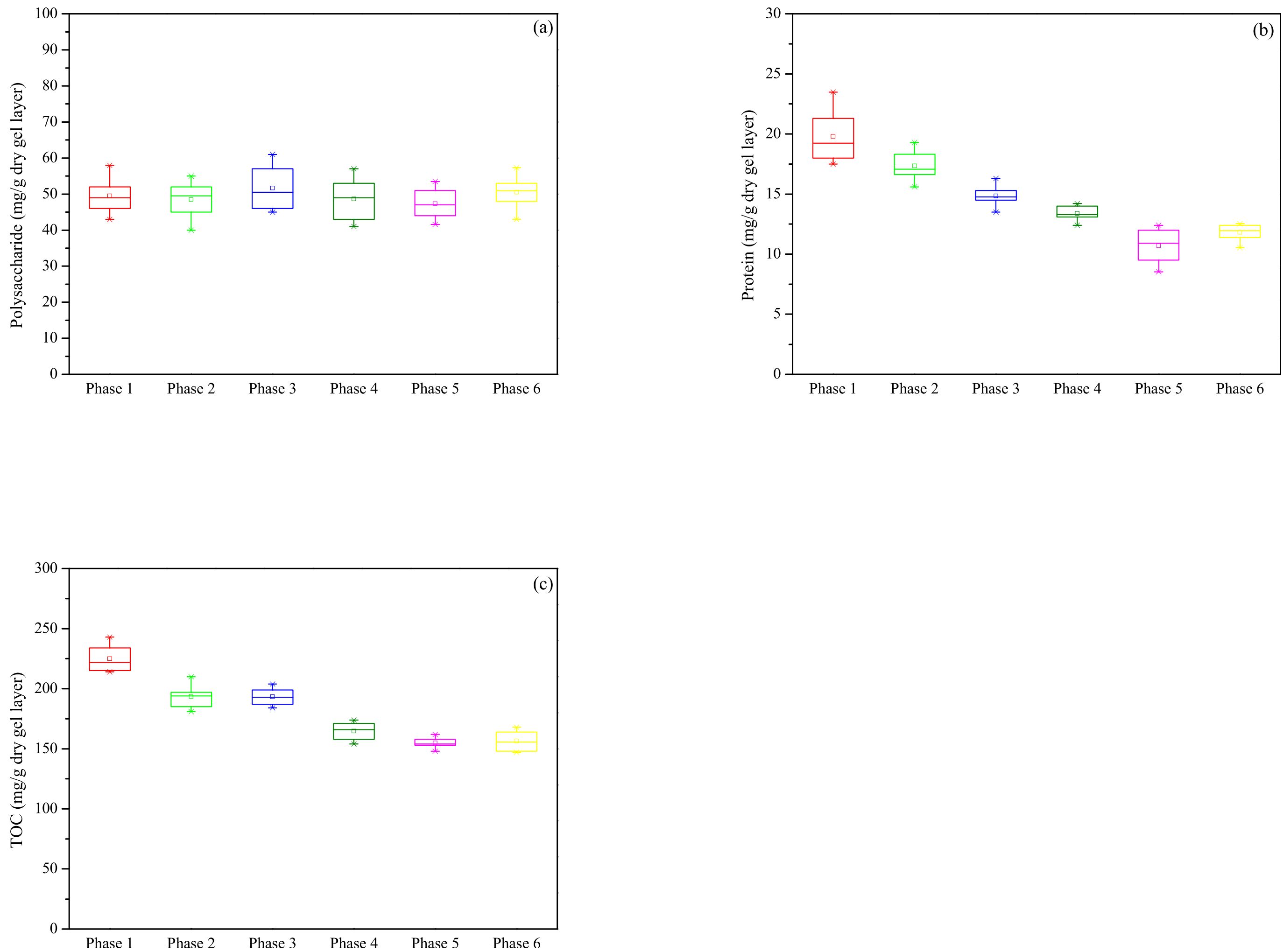

Fig. 5. (a) Polysaccharides, (b) protein and (c) TOC variations of gel layer. (Polysaccharides and protein in the influent during each Phase were lower than the minimum of measuring range, indicating that polysaccharides and protein in the influent could be ignored.)

into A/O-MBR, and the influent contained high concentration of DIC. Thus, inorganic components should play a significant role in membrane biofouling process with plum rain season. Element distributions of particles on gel layer surface (Table S1) have already showed that particles on gel layer contained elements of C, N, P, S, Ca, Mg, Fe, Ba, Al and Si, and elements of Al and Si presented the high distribution in gel layer, indicating that those particles should mostly be inorganic components. Thus, Fig. 4 predicted that plum rain season caused inorganic particles largely accumulating on the gel layer surface. XRD results further analyzed the structure of inorganic components in gel layer. Fig. S4(a) shows that gel layer of Phase 2 included SiO_2, $AlPO_4$, $MgSiO_3$, $CaCO_3$, $BaCO_3$ and Al_2O_3. Fig. S4(b) presents that gel layer of Phase 5 contained SiO_2, $AlPO_4$, FeO, $CaCO_3$, $CaAl_2Si_2O_8$, $BaCO_3$, Al_2O_3 and $Ca_3Al_{10}O_{18}$. $CaSO_4$, $FePO_4$, $Ca_2(PO_4)_3$, $Mg_2(PO_4)OH$, etc. were also identified in gel layer of both Phase 2 and Phase 5. It indicates that the structure of inorganic components in gel layer had no obvious variations with plum rain season, which means inorganic variations of membrane biofouling and its gel layer should because of evolution inorganic mass, but not its structure.

Inorganic element distributions of whole gel layer were showed as results of Fig. 6. Ca, Mg, Fe, Ba, Al and Si were the majority of inorganic elements in gel layer during the entire operation. And concentrations of these elements in gel layer obviously increased with plum rain season, which was mostly because that more components of Ca, Mg, Fe, Ba, Al and Si exited in the municipal wastewater during plum rain season and most of them was intercepted in the reactor with membrane (Fig. S6). Additionally, Si was the major inorganic element in gel layer, and presented a gradual weight increase to over 150 mg/(g dry gel layer) with plum rain season, indicating element Si, which was mainly in form of SiO_2, largely accumulated into gel layer during plum rain season. This was because of high concentration of Si components in the influent of municipal wastewater and maintained in the reactor. Previous studies (Zhou et al. 2014, 2015a) have reported that acid rainy weather might cause plenty of SiO_2 flowing into municipal wastewater treatment system, and then led to SiO_2 attached onto membrane surface with connection with −COOH or −OH. Element Al also showed a high weight percentage in gel layer, increasing from 15 to over 25 mg/(g dry gel layer), with rainy weather. As previous reports (Zhou et al., 2015a, 2017a), elements of Si and Al were normally in the form of SiO_2−Al_2O_3 crystal, and XRD results also show gel layer in this study contained both SiO_2 and Al_2O_3, predicting that plenty of SiO_2 accumulation into gel layer would be strongly accompanied by element Al contribution to gel layer formation. Additionally, high p*Ksp* of $AlPO_3$ (20.01) means increasing Al^{3+} with rainy weather would easily precipitate with PO_4^{3-} in the reactor. Therefore, gel layer contained high concentration of Al.

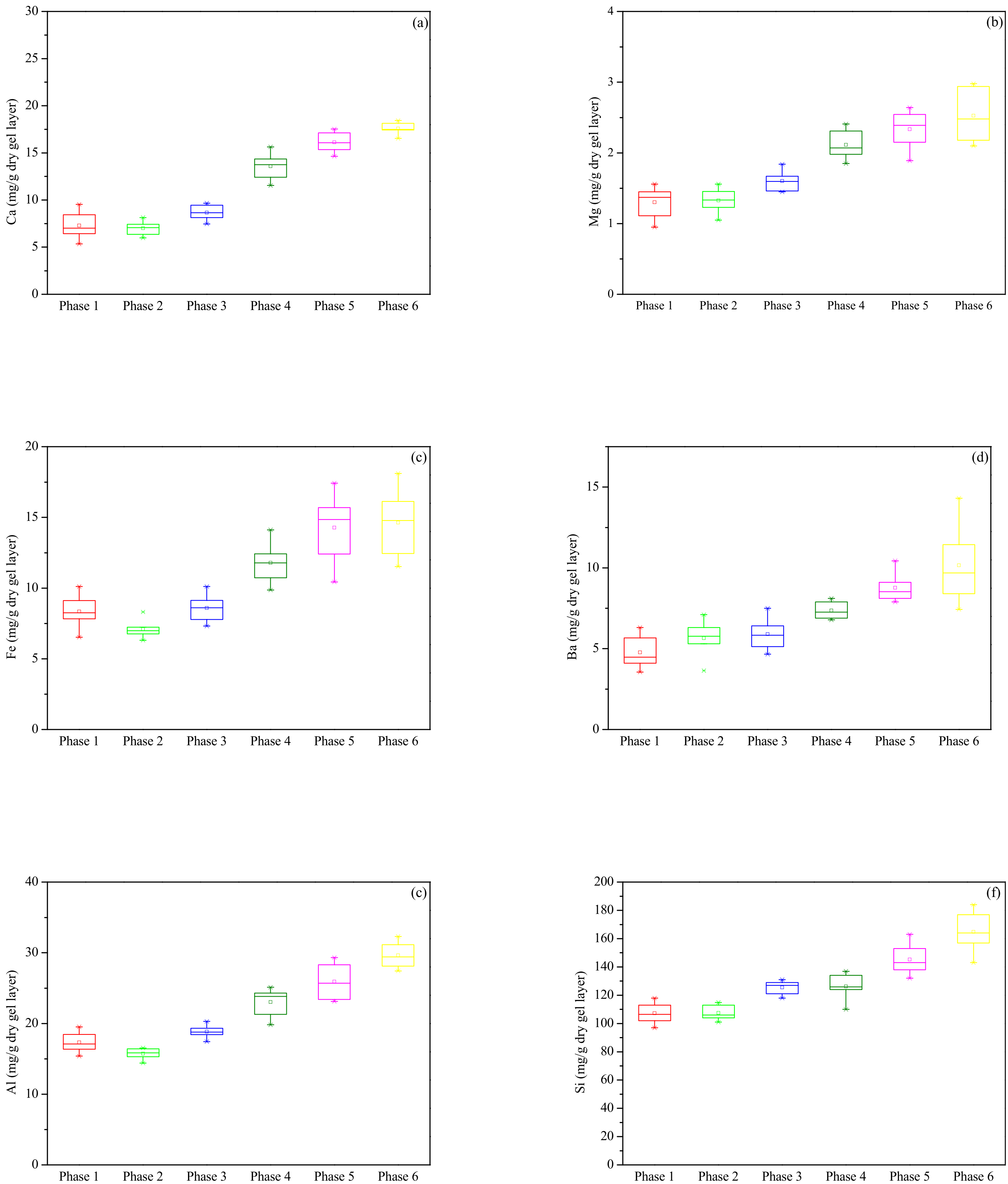

Fig. 6. Element distribution of whole gel layer: (a) Ca; (b) Mg; (c) Fe; (d) Ba; (e) Al; (f) Si.

Moreover, Fig. 1 obviously shows that DIC, most of which should be HCO_3^- and CO_3^{2-}, had an increase from 2 to over 10 mg/L in the influent, and correspondingly stable TP in effluent indicated mixed liquid contained around 2 mg/L TP (most of TP should be in the form of PO_4^{3-}) during the entire operation. Based on solubility product constants (Table 2), elements of Ca, Mg, Fe, Ba and Al easily react with HCO_3^-, CO_3^{2-} and PO_4^{3-}. Therefore, gel layer had the obvious weight increase of element Ca, Mg Ba and Fe, which were

Table 2
Solubility product constants (Speight, 1998).

Compound	p*K*sp	Compound	p*K*sp	Compound	p*K*sp	Compound	p*K*sp	Compound	p*K*sp
$CaCO_3$	8.54	$MgNH_4PO_4$	12.60	$Fe(OH)_3$	38.5	$BaCO_3$	8.59	$AlPO_4$	20.01
$Ca[Mg(CO_3)_2]$	11	$MgCO_3$	5.17	$FePO_4$	15.00	$BaHPO_4$	6.49	$AlsS_3$	6.70
$CaHPO_4$	7.00	$Mg(OH)_2$	11.25	FeS	17.20	$BaSO_4$	9.97		
$Ca(OH)_2$	5.26	$Mg_3(PO_4)_2$	23.98	$FeCO_3$	10.50	$BaSO_3$	9.30		
$CaSiO_3$	7.60								
$CaSO_3$	7.17								

in the form of $CaCO_3$, $CaSiO_3$, $MgNH_4PO_4$, $BaCO_3$, $AlPO_4$ etc. In other words, strong precipitation reaction happened with plum rain season, and plenty of inorganic sediments were found and cleaned at the reactor bottom during entire operation, especially with plum rain season. Precipitate were easily forced through membrane pores under suction pressure, and small-size particles would induce the severe pore blocking. Consequently, plum rain season enhanced pore blocking behavior and led to serious membrane biofouling, but with the inhibition of gel layer formation.

In practice, large-scale MBRs for megacity municipal wastewater treatment in Yangtze River Delta showed the similar results as the laboratory-scale one in this study. Hu et al. (2014) reported that the large-scale MBR (Hefei, China) with 50,000 m^3/d capacity had the increase of TMP development rate from 0.28 to 0.59 kPa/d during plum rain season, even with SS increase but pollutant (COD_{Cr}, NH_4^+-N, TP, etc.) decrease in the influent of municipal wastewater. Additionally, many pilot and large scale MBR studies proved that EPS in gel layer and mixed liquor had the directly positive relationship with membrane biofouling (Meng et al., 2017; Wang et al., 2008). However, during plum rain season, because of pollutant decrease in the influent, not only laboratory-scale MBR in this study but also other four large-scale MBRs in Wuxi (Shen et al., 2012; Sun et al., 2015) showed the obvious decrease of EPS in gel layer and/or mixed liquor, but severer membrane biofouling. Therefore, based on the above analysis in this study and the similar performance of large-scale MBRs for megacity municipal wastewater treatment in Yangtze River Delta, plum rain season could lead to severer biofouling with pore blocking due to inorganic component increase in the influent, even with lower EPS in gel layer and mixed liquor. According to the assessment of membrane biofouling and its gel layer in this study, inorganic component biofouling behavior should be considered as the important role in the membrane biofouling of MBR operation, and inorganic component removal in the influent (such as coagulation, chemical precipitation, etc.) would be the effective pretreatment for membrane biofouling mitigation during plum rain season in Yangtze River Delta.

4. Conclusions

Membrane biofouling and its gel layer of A/O-MBR for megacity municipal wastewater treatment during plum rain season in Yangtze River Delta, China, was assessed in this study. During April–July operation of A/O-MBR, COD_{Cr}, NH_4^+-N, TN, TP of the influent gradually decreased during plum rain season, and inhibited pollutant removal due to organic carbon shortage. However, DIC and inorganic components in mixed liquid had an obvious increase under rainy weather. Results of TMP and membrane resistance indicated that plum rain season enhanced pore blocking behavior, further leading to the severe membrane biofouling but inhibiting gel layer formation. Additionally, gel layer analysis predicted that plum rain season led to plenty of inorganic components and precipitate flew into A/O-MBR reactor. Elements of Ca, Mg Ba, Fe, Al and Si blocked membrane pores, and accumulated into gel layer in the form of SiO_2, $CaCO_3$, $CaSiO_3$, $MgNH_4PO_4$, $BaCO_3$, $AlPO_4$ etc. Consequently, plum rain season enhanced pore blocking behavior and led to serious membrane biofouling but with the inhibition of gel layer formation.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.watres.2017.10.004.

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